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# Comparative Analysis of Properties of the Carbon-Based Coatings Obtained through Various PVD and CVD Deposition Methods

D V Korzhenko<sup>1</sup>, Y N Yurjev<sup>1,2</sup>, D R Emlin<sup>3,7</sup>, S A Plotnikov<sup>4</sup>, A B Vladimirov<sup>4</sup>, I Y Romanov<sup>3</sup>, B A Loginov<sup>5</sup> and A B Loginov<sup>6</sup>

<sup>1</sup>National Research Tomsk Polytechnic University, Tomsk, Russia

<sup>2</sup>Institute of Atmospheric Optics of the Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia

<sup>3</sup>Institute of Electrophysics of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia

<sup>4</sup>Institute of Metal Physics of the Ural Division of the Russian Academy of Sciences, Ekaterinburg, Russia

<sup>5</sup>National Research University of Electronic Technology, Moscow, Russia

<sup>6</sup>Lomonosov Moscow State University, Moscow, Russia

<sup>7</sup>Ural Federal University, Ekaterinburg, Russia

E-mail: dman@tpu.ru

**Abstract.** The paper examines carbon 0.5-1 $\mu$  thick coatings obtained through various physical vapour deposition and chemical vapour deposition methods on stainless steel and tool steel substrates. Their composition, morphology and physical properties have also been studied. The correlations of erosive wear resistance and  $H^3/E^2$  ratio (where  $H$  is hardness and  $E$  is elastic modulus) have been identified for carbon coatings in regards to the production method. Ta-C carbon coatings demonstrate high resistance to dynamic loads with erosive wear in a sand-blast machine.

## 1. Introduction

Industrial development requires the continuous improvement of properties of various parts and mechanisms, in particular increasing the service life under extreme loads, operation in aggressive media without applying grease. Specific strict requirements are set for the parts which have various contact action: friction, rolling friction etc. One way to improve the properties of such products is to create on their surface a modified layer of protective material with high hardness, low friction coefficient, good thermal stability, and resistance to aggressive media. The coatings should possess low erosive wear, its value correlating with higher hardness of coating material, and demonstrate high endurance which usually corresponds to higher values of Young's modulus. Micro- and nanoindentation is widely used to estimate mechanical strength, elastic and plastic properties of the coating material. Using the method proposed by the authors [1], the values of hardness  $H_v$  and Young's modulus  $E$  are calculated based on the load-unload curves. The ratio  $H/E$  describes the resistance of coating material to elastic collapse failure (plasticity index), while the ratio  $H^3/E^2$  is used



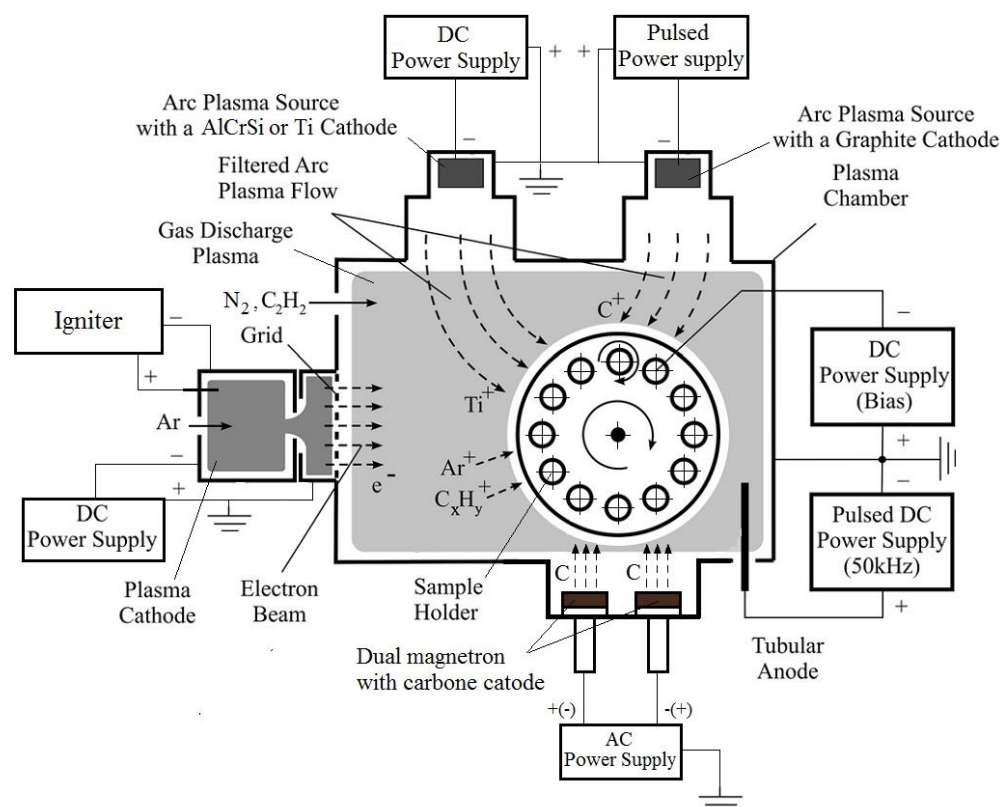
to identify plastic resistance of the material [2]. So, to improve elastic collapse failure and reduce plastic deformation, the coating material should possess high hardness and a small Young's modulus value. Thin carbon-based films (diamond-like films) are one of such protective coatings the properties of which (including the  $H/E$  ratio) may vary within a large range depending on the method and conditions of production.

Nowadays there are two main techniques to obtain carbon diamond-like coatings which are as follows: physical vapour deposition (PVD) including cathodic arc deposition [2, 3], magnetron sputtering [4, 5] etc.; and chemical vapour deposition (CVD) based on decomposition of hydrocarbon-containing gases using various types of discharge [6]. When applying the first two techniques, tetrahedral carbon (ta-C) and amorphous carbon (a-C) referred to as hydrogen-free coating are obtained respectively. CVD method is used to deposit films of hydrogenated amorphous carbon (a-C:H) [7].

This paper is devoted to comparing properties of carbon-based coatings obtained through PVD and CVD.

## 2. Materials and methods

The films were obtained on special equipment, which provided cleaning of substrates surface with ion bombardment and subsequent deposition of metal and carbon coatings in one vacuum process. It consists of an operating chamber with a volume of approximately  $0.1 \text{ m}^3$ , in which there are a planetary substrate holder with diameter 500 mm for 60 samples, and a two-stage vacuum pumping system which provides residual pressure of no less than  $5 \cdot 10^{-3} \text{ Pa}$ . The equipment includes a cathodic arc plasma source with metal cathode, impulse-arc plasma source with graphite cathode [8], dual magnetron sputtering system [9], and the source of low-energy electron beam on the basis of a self-sustained glow discharge maintaining assisted discharge (frequency 50 kHz) in the operating chamber within a wide range of voltage. The flow chart of the device is in the figure 1.



**Figure 1.** Flow chart of the experimental facility.

All coatings were deposited on R6M5 (HS6-5-2) steel and 12X18H10T (AISI 321) stainless steel samples. Before deposition, all samples were cleaned in ultrasound bath in the mixture of ethylic alcohol and rubber solvent. Then samples were bombarded by argon ions from ion source *Radikal* ( $U_a = 3$  kV,  $I_a = 0.25$  A,  $P_{Ar} = 0.05$  Pa) with pulse bias voltage on the substrate (50 kHz)  $U_b = 300$ - 1500 V.

### 2.1. Deposition of ta-C coatings

A sublayer of titanium 50 nm thick was applied to deposit diamond-like coatings (ta-C) 0.7  $\mu$  thick after cleaning samples with arc sputtering, with gradual reduction of voltage  $U_b$  from 500 V to 0 V. Then, a gradient sublayer was applied with coevaporation of carbon from vacuum arc discharge on the surface of graphite target with gradual increasing frequency of pulse-recurrence rate from 3 to 15 Hz and Ti from plasma of continuous separated arc. The thickness of transition layer was approximately 50 nm and the layer composition gradually changed from 0 to 50 % of carbon. After that, the deposition of diamond-like coating continued with residual pressure of  $5 \cdot 10^{-3}$  Pa. The energy of carbon ions was 90 eV. The deposition rate of diamond-like coating was 0.05 Angstrom per impulse.

### 2.2. Deposition of a-C:H coatings

Hydrogenated a-C:H coatings 1  $\mu$  thick were deposited with  $C_2H_2$  acetylene decomposition in plasma of argon-acetylene high-frequency assisted discharge (50 kHz, 3 A, 300 V) with plasma cathode. Self-sustained glowing discharge in discharge system of plasma cathode with 2 A current was maintained under argon pressure supplied in discharge gap of electron source 0.03 Pa.

Similar to preparing the ta-C coating, a sublayer of titanium  $\sim 50$  nm thick was applied on the surface after cleaning with ion bombardment with reducing  $U_b$ , then a gradient sublayer ( $\sim 50$  nm) was applied by coevaporation of carbon (with vacuum impulse-arc sputtering of graphite) and Ti from plasma of continuous separated arc. The coatings were deposited for 1 hour from decomposing acetylene in plasma of assisted discharge, supplied under partial pressure  $P \sim 0.07$  Pa (30 sccm) under pulse bias voltage on the substrate  $U_b = 300$  V which was selected according to the data given by the authors [2], who highlighted the correlation of properties, in particular of hardness, a-C:H coatings and voltage of assisted discharge. The deposition conditions of a-C:H coating were selected to provide production of coatings with the highest hardness.

### 2.3. Deposition of a-C coatings

The a-C coatings 0.5  $\mu$  thick were obtained with dual magnetron sputtering system during sputtering of graphite target in argon plasma. The pressure of argon during deposition was 0.19 Pa, operating pressure was 870 V, discharge power was 4.5 kW. The deposition rate was 0.5  $\mu$  per hour. Ti 50 nm thick film was used as a sublayer.

The temperature of all samples did not exceed 200°C during deposition.

### 2.4. Test equipment

The paper examined various mechanical properties of carbon films and the morphology of their surface. Microhardness tester *DUH 211S Ultramicro hardness tester* (Shimadzu, Japan) was used to gauge microhardness with 50 mN indentation load, nanohardness tester *NANO Hardness Tester NHT-S-AX-000X* (CSEM, Switzerland) was used to gauge nanohardness with 10mN indentation load. Berkovich indenter was applied in both testers. The optical microscope of the latter tester was used to obtain images of film surface with x50, x200 and x1000 zoom.

The morphology and average roughness  $R_a$  of the surface were estimated according to the results of atomic force microscopy in contact mode. The research was carried out on scanning probe microscope *SMM-2000* (Proton-MIET, Russia). The scan area was  $17.6 \times 17.6 \mu^2$  and  $1 \times 1 \mu^2$  to estimate general morphology of surface and its structure correspondingly. Simple average roughness  $R_a$  was calculated as the integrated profile of rectangular area of two-dimensional scan with microscope software. Tribometer produced by CSEM with an indenter in the form of a tungsten bulb was used to gauge the friction coefficient and tested coating samples for wear at constant load of 5 N. Test cycle was 1000

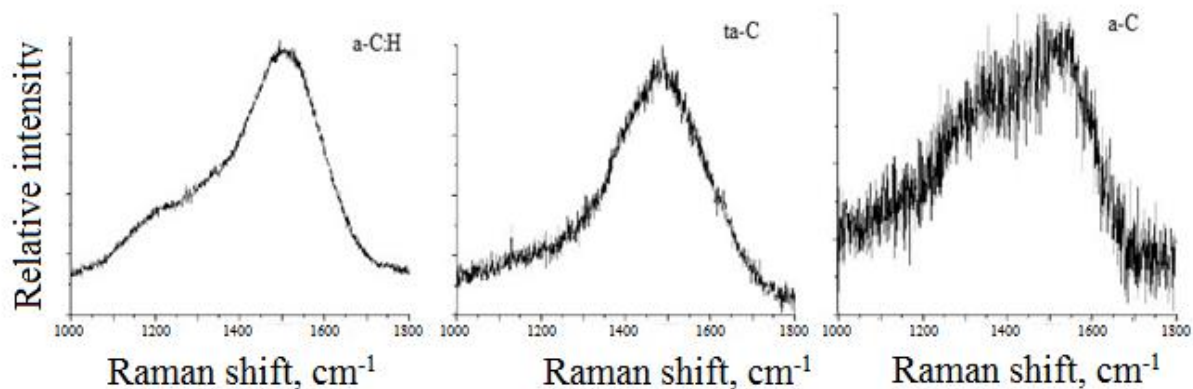
rotations of the sample about itself. The area of the track left by the bulb on the sample was gauged using optical three-dimensional non-contact profilometer *Micro Measure 3D Station* (STIL SAS, France).

Erosive wear resistance of the samples with coatings was studied with a special rotor-type installation for erosive wear [7]. The samples were bombarded with corundum particles of approximately 100  $\mu$  in diameter at the speed of 10 m/s at an angle of 90° to the surface. The samples were weighed at regular intervals after the bombarding solid particles reached certain mass, which allowed developing the correlations between the sample weight loss  $m$  and the quantity of the abrasive powder used  $M$ .

The phase composition of films was examined with Raman spectroscopy on *Centaur UHR* (Nano Scan Technology, Russia).

### 3. Results and discussion

Gauging phase composition of the films obtained with Raman spectroscopy shown in figure 2 have demonstrated that the obtained spectra are typical of each type of carbon diamond-like coatings [10].



**Figure 2.** Spectra of Raman scattering of the coatings.

The results of processing Raman spectra according to the technique described by Ferrari [11] are in the Table 1. The analysis of Raman spectra has shown that the obtained coatings have typical structure and estimated content of  $sp^2$  and  $sp^3$  phase which largely determines their physical and operational properties. So, the least amount of diamond-like bonds is in a-C and a-C:H films (30 and 40 % correspondingly), while ta-C coating contains more than 70% of diamond-like bonds.

**Table1.** Parameters of D and G peaks of carbon films Raman spectra.

| Film type | G peak position (cm <sup>-1</sup> ) | FWHM <sup>a</sup> (G)(cm <sup>-1</sup> ) | D peak position (cm <sup>-1</sup> ) | FWHM (D) (cm <sup>-1</sup> ) | I <sub>D</sub> /I <sub>G</sub> <sup>b</sup> | Content sp <sup>3</sup> (%) |
|-----------|-------------------------------------|--|-------------------------------------|------------------------------|---|-----------------------------|
| ta-C      | 1557                                | 230                                      | 1343                                | 446                          | 0.26  | 70-80                       |
| a-C:H     | 1575                                | 105                                      | 1368                                | 353                          | 0.85  | 30-40                       |
| a-C       | 1540                                | 122                                      | 1360                                | 271                          | 0.94  | 20-30                       |

<sup>a</sup>FWHM – full-width-half maximum.

<sup>b</sup>I<sub>D</sub>, I<sub>G</sub> – intensity of D and G peaks correspondingly.

Table 2 shows properties of carbon-based coatings obtained using the abovementioned techniques.

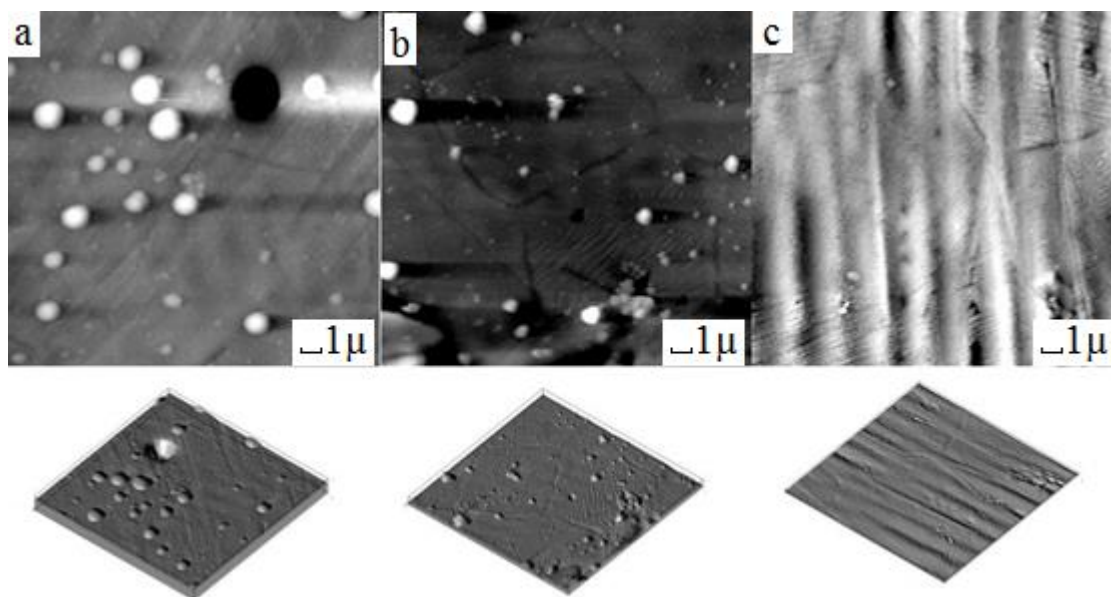
**Table 2.** Properties of the coatings.

| Property/coating                |                              | a-C:H     | ta-C    | a-C      |
|---------------------------------|------------------------------|-----------|---------|----------|
| Nanohardness (10 mN), $N$ , GPa |                              | 17.5      | 17.3    | 17.5     |
| Young's modulus, $E$ , GPa      |                              | 220       | 150     | 180      |
| $H/E$                           |                              | 0.08      | 0.11    | 0.09     |
| $H^3/E^2$                       |                              | 0.11      | 0.22    | 0.17     |
| Roughness,                      | Profilometer, 11 mm          | 48        | 30      | 118      |
| $R_a$ , nm                      | Image, 17.6x17.6 $\mu$       | 25.3      | 28.8    | 18.3     |
| Scanning area                   | Image, 1x1 $\mu$             | 4.1       | 1.6     | 2.4      |
| Clusters size, nm,              | On the image 17.6x17.6 $\mu$ | 480       | 360     | >1000    |
|                                 | On the image 1x1 $\mu$       | appr. 160 | appr. 5 | appr. 80 |
| Friction coefficient,           | initial $f_s$                | 0.19      | 0.38    | 0.15     |
|                                 | after grinding $f_i$         | 0.12      | 0.08    | 0.11     |
| Wear area, $S$ , $\mu^2$        |                              | <1        | 20      | <1       |

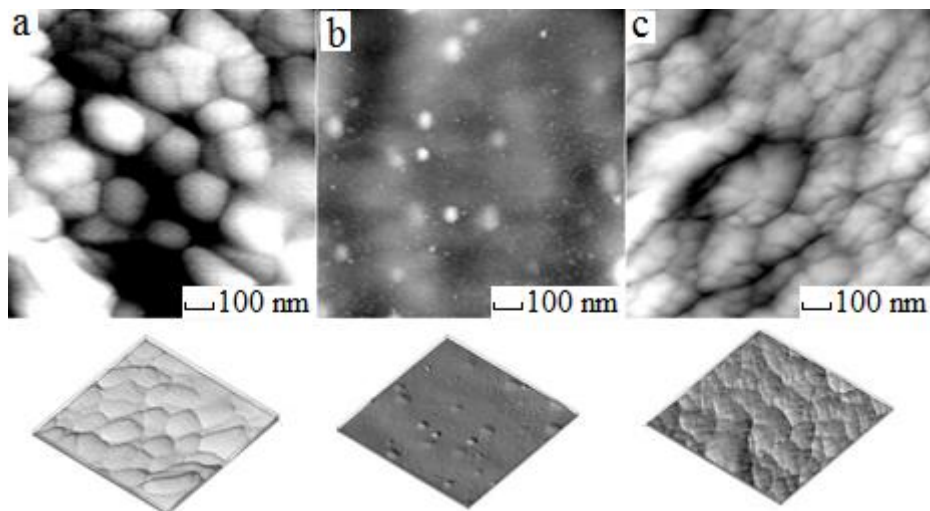
As it can be inferred from the data, nanohardness of all types of the coatings (load 10mN) is close enough and is 17.5 GPa. Low hardness of diamond-like films of all types at this load can be attributed to heterogeneity of the surface (cluster films of typical cluster size is approximately 100 nm) (Table 1, figure 3 and 4). Three-dimensional island regions on the surface of films are outcrops for some clusters. The coatings surface geometry (360 nm for ta-C, 480 nm for a-C:H and 500 nm for a-C coatings) greatly exceeds the size of crystalline grains which is about 10 nm. Deposition of films is followed by formation of dimples and intercluster edges, which leads to reduction of total surface energy [12]. Such areas have the least density of the coating material, and consequently this leads to the decrease of average microhardness of all types of coatings.

The values of Young's modulus for all coatings varies insufficiently from 150 GPa for ta-C coatings to 220 GPa for a-C:H coatings. Therefore, with this experimental installation it is possible to obtain solid carbon coating with approximately similar hardness which differ in the value of Young's modulus. From the point of view of wear resistance, ta-C coating appears to be the most perspective (the ratios  $H/E$  and  $H^3/E^2$  are 0.11 and 0.22 correspondingly (see Table 2) than a-C:H and a-C coatings.

Gauging the friction coefficient has demonstrated that there are insignificant differences for a-C:H, ta-C and a-C coatings (figures 3, 4). High values of friction coefficient are typical on the initial stage, with fast decrease to values typical of diamond-like films (<0.1) [11].

**Figure3.** Microphotographs 17.6x17.6 $\mu$  and 3d sample surface models: a) a-C:H, b) ta-C, c) a-C.



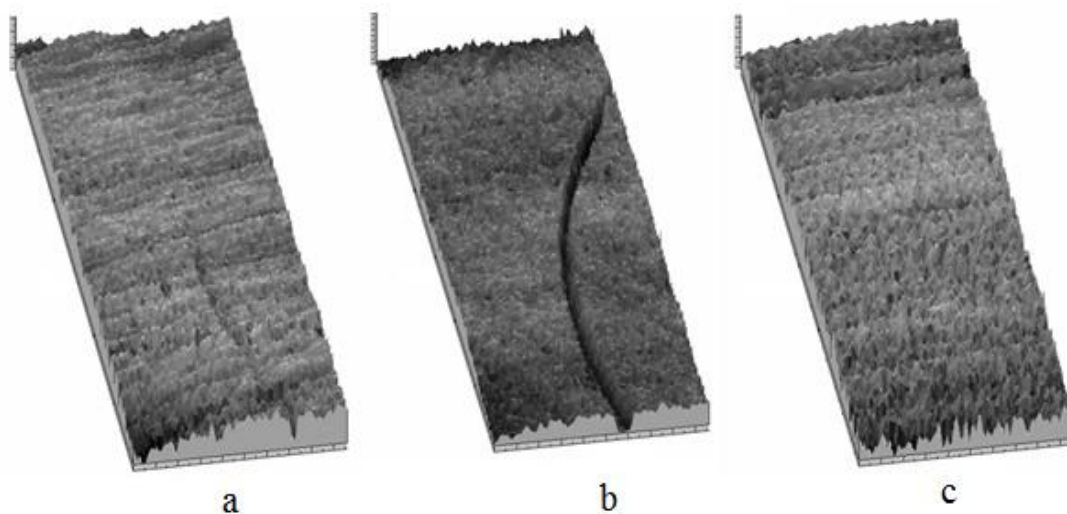


**Figure 4.** Microphotographs  $1 \times 1 \mu$  and 3d sample surface models: a) a-C:H, b) ta-C, c) a-C

Atomic force microscopy demonstrates significant differences between coating obtained through various techniques. Films a-C:H and a-C (figure 3 a, d) possess the values of roughness which are close enough, though since a-C coating is less thick, the impact of the substrate on the geometry is more noticeable. The image  $1 \times 1 \mu$  shows that a bit more detailed structure is formed during magnetron sputtering than during deposition from plasma (figure 4 a, c), which explains a bit larger  $R_a$  value. On the whole, films of both types are homogeneous enough and have similar morphology and roughness.

The presence of a dense structure without pronounced heterogeneities and intercluster edges leads to ta-C coatings (figure 3c) having the least values of  $R_a$  roughness. However, it is important to note that the given values correspond the areas of film that is free of large particles. In a more general view of the surface it can be seen that it is covered with numerous projections of 200-400 nm, taking which into account the average roughness of the surface  $R_a$  can increase from 1.6 to 28.8 nm. These projections consisting of carbon with mainly  $sp^2$ -bonds is the result of graphite sputtering in the arc and the presence of a flow of large clusters of cathode material on the surface of the parts in the absence of magnetic separation of ionic flux [12].

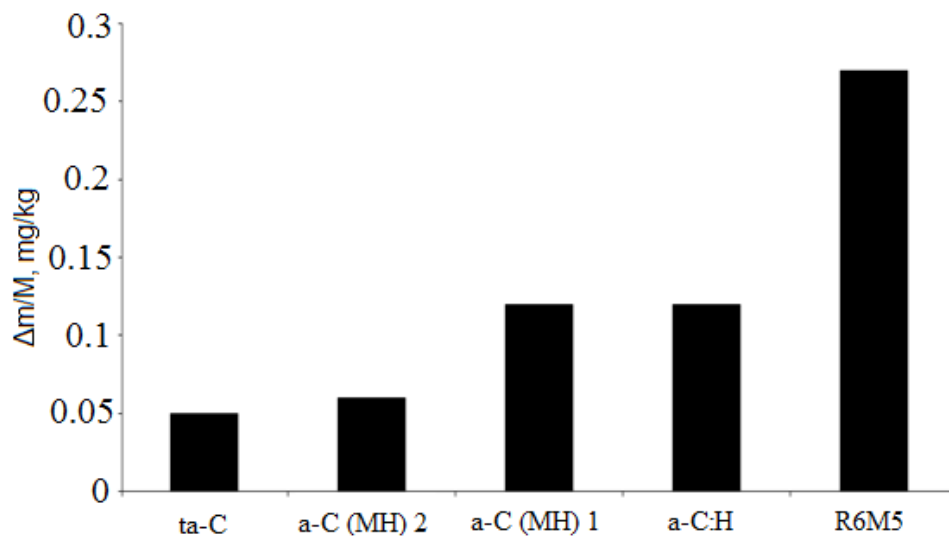
Figure 5 shows 3d models of the track areas left by the indenter of tribometer during gauging wear and friction coefficient.



**Figure 5.** 3d model of the surface with an imprint of the tribometer indenter trace:  
a) a-C:H, b) ta-C, c) a-C.

Figure 5 shows that with similar load on the tribometer indenter equal to 5N the coatings behaved differently. So, there has been left almost no trace of the indenter on the a-C and a-C:H films. Their friction coefficient was similar and equal to 0.11, so it was not possible to identify the wear area for these samples. This behavior of the films might be caused by a larger content of  $sp^2$  bonds and mainly two-dimensional orientation of atoms. Ta-C film also has low friction coefficient which is 0.11, but in this case the wear area was  $58 \mu^2$ . This might be due to the fact that, as noted above, there are individual carbon formations on the coating surface which increase its roughness and because of higher internal stresses they are typical of solid coatings.

The diagram of wear of the samples after testing them in a sand-blast machine is in figure 6.



**Figure 6.** The diagram of wear of the films surface after processing in a sand-blast machine.

Figure 6 demonstrates that blank substrate is exposed to largest wear. Coatings a-C and a-C:H have quite similar values and decrease the wear of the original substrate almost two fold. The ta-C coating possesses the highest resistance to erosive wear which is related to the largest resistance of the material to plastic deformation (the ratio  $H^3/E^2 = 0.22$ ).

#### 4. Conclusions

Based on the results given above, it can be inferred that operational properties of carbon-based thin film coatings such as wear resistance may vary selecting the appropriate technique for their deposition. So, softer a-C and a-C:H coatings obtained through magnetron deposition and assisted glowing discharge correspondingly have smaller roughness and contain more graphite-like  $sp^2$  bonds which are grease for static friction. This provides higher resistance of these coatings to such loads if compared to ta-C coatings. Using a-C and a-C:H films also allows reducing the wear of the original substrate almost twofold under dynamic loads by the example of exposure to sand in a sand-blast machine.

The ta-C film has maximum hardness of all carbon coatings and average surface roughness. This determined its maximum resistance to dynamic loads in a sand-blast machine. Reduction of surface wear is observed by more than four times.

Thus, a carbon-based protective coating should be chosen according to the load expected. Softer a-C and a-C:H coatings are more resistant under static loads than ta-C coatings to dynamic ones (under the action of abrasive material). It is obviously reasonable to use a combination of hard and soft coating when there are two types of loads. Such multilayer coatings have a number of advantages, the most important of which are high hardness and low Young's modulus. Therefore, we can expect high wear resistance.



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